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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : C09K 7/02, E21B 37/06	A1	(11) International Publication Number: <b>WO 96/04348</b> (43) International Publication Date: 15 February 1996 (15.02.96)
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(21) International Application Number: PCT/US95/09443

(22) International Filing Date: 26 July 1995 (26.07.95)

(30) Priority Data:  
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P.O. Box 4740, Houston, TX 77210-4740 (US).(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH,  
CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG,  
KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW,  
MX, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT,  
UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES,  
FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent  
(BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD,  
TG), ARIPO patent (KE, MW, SD, SZ, UG).

Published

*With international search report.*(54) Title: DRILLING FLUID ADDITIVES FOR HYDRATE PRONE ENVIRONMENTS HAVING WATER-SENSITIVE MATERIALS,  
DRILLING FLUIDS MADE THEREOF, AND METHOD OF DRILLING HYDRATE PRONE ENVIRONMENTS HAVING  
WATER-SENSITIVE MATERIALS

## (57) Abstract

Disclosed is a drilling fluid additive which includes a polymer component and a hydrate suppression component. Examples of the polymer component include polyvinylalcohol, polyvinylpyrrolidone, polymer of styrene sulfonic acid, cationic polymers, terpolymers of acrylamide, acrylate, acrylamide propane sulfonic acid, and polyvinylpyrrolidone copolymers. Examples of the hydrate suppression component broadly include alcohols and salts. Also disclosed is a water-based drilling fluid which, in addition to an aqueous component, includes the additive described above. Additionally disclosed is a method of drilling in a hydrate prone environment containing water-sensitive shales, clays and fines using the drilling fluid described above.

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DRILLING FLUID ADDITIVES FOR HYDRATE PRONE ENVIRONMENTS HAVING  
WATER-SENSITIVE MATERIALS, DRILLING FLUIDS MADE THEREOF, AND  
METHOD OF DRILLING HYDRATE PRONE ENVIRONMENTS HAVING WATER  
SENSITIVE MATERIALS

Field of the Invention

The present invention relates to drilling fluid additives, to drilling fluids, and to  
methods of drilling. In another aspect, the present invention relates to drilling fluid  
additives for use in those environments prone to hydrate formation, to drilling fluids  
for use in hydrate prone environments, and to methods of drilling in hydrate prone  
environments. In still another aspect, the present invention relates to drilling fluid  
additives for use in those environments prone to hydrate formation and which  
contain water-sensitive shales, clays and other fines, to drilling fluids for use in such  
environments, and to methods of drilling in such environments. In even another  
aspect, the present invention relates to drilling fluid additives for use in deep water  
environments having water-sensitive shales, clays and other fines, to drilling fluids  
for use in such environments, and to methods of drilling in such environments.

Description of the Related Art

Drilling in hydrate prone environments having water-sensitive shales, clays  
and other fines presents two major problems to be addressed by the proper  
selection of a drilling fluid: the swelling and migration of these water-sensitive  
shales, clays and other fines; and the formation of hydrates. While it is desirable  
for a drilling fluid to address both of these problems, the prior art drilling fluids have  
addressed only one or the other of these problems.

5       The first major problem is that oil and gas well drilling, production and treating operations are many times hindered by the presence of water-sensitive shales, clays and other fines capable of swelling and/or migrating in the formation upon their interaction with water-based well fluids. The shales, clays and fines may be already present or may be introduced into the formation during drilling,  
10   production or treating activity. In some instances, the shales, clays and fines are quiescent causing no obstruction to the flow of hydrocarbons through the subterranean formation, or interference with drilling activities. However, when water-sensitive shales, clays or fines are disturbed with a water-based well fluid, they can swell and disperse and interfere with drilling, production or treating  
15   operations.

U.S. Patent No. 5,076,373, issued December 31, 1991 to Hale et al., discloses a shale stabilizing drilling fluid comprising an acrylic polyol, a monoalicyclicpolyol or a cyclicetherpolyol, and a partially hydrolyzed polyacrylamide with 20 to 50 percent hydrolysis.

20       The second major problem is the formation of gas hydrates which may interfere with well operations. Gas hydrates are ice-like crystalline solids formed from light gases and water, which can form in aqueous systems at temperatures well above the freezing point of water if the pressure is sufficiently high.

Hydrates were first documented in the early 1800's and introduced to the  
25   petroleum industry in the early 1930's as the culprit responsible for the freezing of gas transmission lines

Hydrates are known as "clathrates" since they consist of "host" water molecules forming a lattice structure acting like a cage to entrap "guest" gas

5 molecules. Light hydrocarbon gases such as methane, ethane, propane, butane, and other gases such as hydrogen sulfide and carbon dioxide are known to produce hydrates with water. Hydrocarbons larger than n-butane cannot form hydrates with water due to limited "host" molecule cage size. See, SPE/IADC Paper No. 16130, "Formation of Hydrates During Deepwater Drilling Operations", Barker et al., 1987  
10 SPE/IADC Drilling Conference, at 703-711.

During the last few years, hydrocarbon drilling and production efforts have continued to expand into deeper waters in many parts of the world. The environment of deep water drilling is one of higher seafloor hydrostatic pressures and lower ambient temperatures. Unfortunately, such higher seafloor hydrostatic  
15 pressures and lower ambient temperatures, greatly increase the chances of hydrate formation at some point in the drilling operation. Thus, it is only recently that hydrate formation during drilling has become a concern.

In fact, actual formation of hydrates during drilling operations has been reported, with the formed hydrates plugging subsea equipment and causing  
20 considerable difficulties in subsequent operations. Barker et al. disclosed hydrates forming in well drilled off the U.S. West Coast in 1150 feet of water with a sea-floor temperature of 45°F, and in a well drilled in the Gulf of Mexico in 3100 feet of water with a seafloor temperature near 40°F.

Potential difficulties in subsea operations include: the formation of a gas  
25 hydrate plug in the ram cavity of a closed blow out preventer ("BOP") preventing it from fully opening; formation of an annular plug between the drill string and the blow out preventers which prevents full BOP closure; plugging of the choke and kill lines preventing their use in well circulation; formation of a plug around the drill string in

5 the riser, BOPs or casing which prevents drilling string movement, and plugging at or below the blow out preventers which prevents the monitoring of well pressure below the BOPs. See, SPE/IADC Paper No. 18638, "Inhibition of Gas Hydrates in Deepwater Drilling", Hale et al., 1989 SPE/IADC Drilling Conference at 195-203. And see, SPE/IADC Paper No. 16130 at 706.

10 Hydrates present a problem, not only of plugging drilling operations, but also additional problems when the hydrate dissociates. A cubic foot of hydrate may contain as much as 170 standard cubic foot of gas. Thus, when a hydrate dissociates due to reduced pressure and/or increased temperature, this trapped gas is then released. The release of large quantities of gas near the surface during  
15 hydrate dissociation could create a dangerous well-control situation. For example, if a hydrate were to dissociate in a limited volume sealed container, such as a core barrel, very high pressures can be generated which could rupture the container.

Various suggestions have been made in the prior art for drilling fluid additives that will hinder or prevent hydration formation.

20 Hale et al., in SPE/IADC Paper No. 18638, suggest the use of sodium chloride and/or glycerol mixtures in a spotting fluid for deepwater drilling.

Lai et al., "Investigation of Natural Gas Hydrates in Various Drilling Fluids", SPE/IADC Paper No. 18637 at 181-194, disclose the use of sodium chloride, glycerine and propylene glycol to lower hydrate formation, and teach away from the  
25 use of other salts as they "tend to be less compatible with standard mud products."

However, while sodium chloride has been suggested as an additive for water-based drilling fluids to depress the hydrate formation temperature, its use is

5 discouraged as corrosion rates tend to be high with such sodium chloride-containing drilling fluids.

Grigg et al., "Oil-Base Drilling Mud as a Gas Hydrates Inhibitor", SPE Paper No. 19560 at 421-432, disclose a calcium chloride containing oil-based drilling mud.

While drilling fluids have been proposed for drilling in formations having  
10 water-sensitive shales, clays or fines, these drilling fluids may not be suitable for hydrate prone environments. Likewise, drilling fluids proposed for hydrate prone environments may not be suitable for drilling in formations having water-sensitive shales, clays or fines. The solution is not as simple as combining the components of such drilling fluids, as the components are many times not suitable with each  
15 other.

For example, as discussed above, partially hydrolyzed polyacrylamide has been suggested for water-based drilling fluids for drilling water-sensitive shales, clays or fines. As also disclosed above, calcium chloride has been suggested for oil-based drilling fluids for drilling in hydrate prone environments. The problem arises  
20 when the formation contains water-sensitive shales, clays or fines, and is in a hydrate prone environment. Any partially hydrolyzed polyacrylamide added to the drilling fluid for the water-sensitive shales, clays or fines, is incompatible with any calcium chloride added to the drilling fluid for hydrate formation.

Thus, there exists a need in the art for an improved drilling fluid additive.

25 There also exists a need in the art for an improved drilling fluid.

There exists another need in the art for an improved method of drilling.

There exists still another need in the art for an improved drilling fluid additive for use in drilling in hydrate prone environments.

5           There exists even another need in the art for an improved drilling fluid for use in drilling in hydrate prone environments.

          There exists yet another need in the art for an improved method of drilling in hydrate prone environments.

          There exists even still another need in the art for an improved drilling fluid  
10   additive for use in drilling in hydrate prone environments containing water-sensitive shales, clays or fines.

          There exists even yet another need in the art for an improved drilling fluid for use in drilling in hydrate prone environments containing water-sensitive shales, clays or fines

15           There exists even still yet another need in the art for an improved method of drilling in hydrate prone environments containing water-sensitive shales, clays or fines.

          These and other needs in the art will become readily apparent to those of skill in the art upon review of this specification.

20

#### Summary of the Invention

          It is one object of the present invention to provide an improved drilling fluid additive.

          It is also an object of the present invention to provide an improved drilling  
25   fluid.

          It is another object of the present invention to provide an improved method of drilling.



5 It is still another object of the present invention to provide an improved drilling fluid additive for use in drilling in hydrate prone environments.

It is even another object of the present invention to provide an improved drilling fluid for use in drilling in hydrate prone environments.

10 It is yet another object of the present invention to provide an improved method of drilling in hydrate prone environments.

It is even still another object of the present invention to provide an improved drilling fluid additive for use in drilling in hydrate prone environments containing water-sensitive shales, clays or fines.

15 It is even yet another object of the present invention to provide an improved drilling fluid for use in drilling in hydrate prone environments containing water-sensitive shales, clays or fines.

It is even still yet another object of the present invention to provide an improved method of drilling in hydrate prone environments containing water-sensitive shales, clays or fines.

20 These and other objects of the present invention will become readily apparent to those of skill in the art upon review of this specification.

According to one embodiment of the present invention there is provided a drilling fluid additive which includes a polymer component and a hydrate suppression component.

25 The polymer component of the present invention must generally be water soluble in high salt concentration. The polymer component may be a polymer or copolymers, with copolymer broadly defined as having two or more monomers. Examples of polymers suitable as the polymer component include polyvinylalcohol,

5 polyvinylpyrrolidone, polymer of styrene sulfonic acid, cationic polymers, terpolymers of acrylamide, acrylate and acrylamide propane sulfonic acid ("AMPS").

Copolymers suitable as the polymer component include polyvinylpyrrolidone copolymers. Other polymers may also be utilized.

10 Examples of materials suitable as the hydrate suppression component include alcohols or salts. Examples of suitable salts include calcium, potassium, magnesium and sodium salts. Examples of alcohols suitable as the hydrate suppression component include mono-, di-, tri- and poly-hydric alcohols.

According to another embodiment of the present invention there is provided a water-based drilling fluid which in addition to an aqueous component, includes a  
15 polymer component and a hydrate suppression component. Preferred examples of the polymer component and the hydrate suppression component are as described above.

According to even another embodiment of the present invention there is provided a method of drilling in a hydrate prone environment containing water-  
20 sensitive shales, clays and fines. The method generally includes rotating a drill string to cut a borehole into the earth while circulating a water-based drilling fluid, having a polymer component and a hydrate suppression component, down through the drill string and then up the annulus between the drilling string and the wall of the borehole.

25

#### Detailed Description of the Invention

The drilling fluid additive of the present invention generally includes a polymer component and a hydrate suppression component.

5       The water-based drilling fluid of the present invention generally comprises in addition to an aqueous component, a polymer component and a hydrate suppression component.

10       In the practice of the drilling method of the present invention, the drill string is rotated to cut a borehole into the earth while circulating a water-based drilling fluid, having a polymer component and a hydrate suppression component, down through the drill string and then up the annulus between the drilling string and the wall of the borehole.

15       The polymer component and the hydrate suppression component utilized in the present invention are generally selected to provide compatibility with each other and with the well fluid, to provide suitable shale, clay or fines stabilization, and to inhibit, suppress or delay the formation of gas hydrates.

20       The aqueous medium employed in the well fluids of the present invention may be any kind of water from any source including, but not limited to, fresh water, sea water, water from the subterranean reservoir, sea water, or a natural or synthetic brine.

25       The polymer component of the present invention must generally be water soluble in high salt concentration. The polymer component may be a polymer, copolymers, or mixture thereof, with copolymer broadly defined as having two or more monomers. Suitable polymer components useful in the present invention preferably also have good wetting properties and a reasonable rate of dissolution in water for convenient use in the field. Suitable polymer components should also afford aqueous solutions of low to moderate viscosities as are traditionally used in drilling wells, particularly oil and gas wells. Additionally, it is

5 preferable that the polymer component be capable of encapsulating the water-sensitive shale, clay or other fines. It is also preferable that the polymer component have suitable thermal stability for the environment in which the well fluids are employed. It is also preferable that the polymer component have suitable resistance to hydrolysis under high pH, generally in the range of about 9 to about 11. Where  
10 necessary to achieve proper water solubility and other suitable properties, the polymer component utilized in the present invention may be hydrolyzed. Finally, it is also preferred that the polymer component utilized in the present invention have good tolerance to drilled solids contamination.

Examples of suitable polymer components include polyvinylalcohol,  
15 polyvinylpyrrolidone, polymer of styrene sulfonic acid, cationic polymers, terpolymers of acrylamide, acrylate, acrylamide propane sulfonic acid ("AMPS"), and polyvinylpyrrolidone copolymers. The more preferable polymers useful as the polymer component include polyvinylalcohol, polyvinylpyrrolidone and polyvinylpyrrolidone copolymers. The most preferred polymers useful as the  
20 polymer component are polyvinylalcohol and polyvinylpyrrolidone.

Suitable vinylpyrrolidone copolymers which may be utilized in the present invention include vinylpyrrolidone/styrene sulfonate/acrylic acid copolymer, vinylpyrrolidone/methylmethacrylate copolymer, vinylpyrrolidone/styrene sulfonate copolymer, vinylpyrrolidone/acrylamide propane sulfonic acid ("AMPS") copolymer,  
25 vinylpyrrolidone/AMPS/acrylamide copolymer, vinylpyrrolidone/AMPS/acrylamide/acrylic acid copolymer, vinylpyrrolidone/dimethylamino ethylmethacrylate copolymer, vinylpyrrolidone/acrylamide/acrylic acid copolymer, vinylpyrrolidone/styrene sulfonate/acrylic acid/acrylamide copolymer, vinylpyrrolidone/AMPS/styrene

5 sulfonate copolymer, vinylpyrrolidone/methyl methacrylate/styrene sulfonate copolymer.

Other copolymers which may be utilized in the present invention include styrene sulfonate/methyl methacrylate copolymer, styrene sulfonate/AMPS copolymer, and acrylate/acrylamide/AMPS copolymer.

10 The preferable polymers to utilize in the present invention are polyvinylalcohol and polyvinylpyrrolidone.

The polyvinylalcohol which may be utilized in the present invention may be prepared by any suitable method known to those of skill in the art. The molecular weight of the polyvinylalcohol must be suitable for effective encapsulation of the drill  
15 cuttings and water sensitive shale, clay or fines. The higher end of the molecular weight range is generally dictated by solubility and viscosity limitations. Generally, the average molecular weight of the polyvinylalcohol utilized in the present invention will be at least 50,000, preferably in the range of about 50,000 to about 200,000, more preferably in the range of about 100,000 to about 175,000, and most  
20 preferably in the range of about 125,000 to about 175,000. Polyvinylalcohols suitable for use in the present invention will have a percent hydrolysis of at least 60 percent, and preferably in the range of about 80 to about 99 percent. Polyvinylalcohol may be utilized in solid or solution form.

The polyvinylpyrrolidone utilized in the present invention may be prepared by  
25 any suitable method known to those of skill in the art. The average molecular weight of the polyvinylpyrrolidone must be suitable for effective encapsulation of the drill cuttings and water sensitive shale, clay or fines. The higher end of the molecular weight range is generally dictated by solubility and viscosity limitations.

- 5 Generally, the average molecular weight of the polyvinylpyrrolidone utilized in the present invention will be at least 10000, preferably in the range of about 10000 to about 1,500,000, more preferably in the range of about 500,000 to about 1,200,000, and most preferably in the range of about 750,000 to about 1,000,000.

The vinylpyrrolidone copolymers utilized in the present invention may be  
10 prepared by any suitable method known to those of skill in the art. The average molecular weight of the vinylpyrrolidone copolymer must be suitable for effective encapsulation of the drill cuttings and water sensitive shale, clay or fines. The higher end of the molecular weight range is generally dictated by solubility and viscosity limitations. The average molecular weight of the vinylpyrrolidone  
15 copolymer utilized in the present invention will be in the range of about 200 to about 10,000,000. Preferably the molecular weight of the vinylpyrrolidone copolymer utilized will be in the range of about 500 to about 2,000,000, more preferably in the range of about 1000 to about 1,500,000, and most preferably in the range of about 1000 to about 1,000,000.

- 20 The hydrate suppression component utilized in the present invention may be selected from among alcohols, and certain salts.

The salts which may be utilized as the hydrate suppression component may be selected from among calcium, potassium, magnesium and sodium salts. Preferred examples of such salts include calcium bromide, magnesium bromide,  
25 potassium bromide, calcium chloride, magnesium chloride, potassium chloride, sodium formate and potassium formate. The more preferred salt to use as the hydrate suppression component is calcium chloride.

5 Alcohols which may be utilized as the hydrate suppression component of the present invention are generally selected from among water-soluble or poorly water insoluble alcohols and derivatives thereof. Such water-soluble or poorly water insoluble alcohols include mono-, di-, tri- and poly-hydric alcohols. Non-limiting examples of classes of alcohols suitable for use in the present invention include  
10 glycols, glycerols, sorbitols, and derivatives thereof. Silicone containing alcohols, such as silicone containing glycols are also useful in the present invention.

Alcohols suitable to be utilized in the present invention may be a di-hydroxy alcohols, such as polyalkylene glycols, particularly polypropylene glycol. Suitable alcohols include propoxylated tri-hydroxy alcohols such as polyalkylene glycerols,  
15 particularly polypropylene glycerol. Ethylene oxide propylene oxide copolymers of di-hydroxy and tri-hydroxy alcohols may also be utilized as the alcohol of the present invention.

Polyglycols suitable for use as the hydrate suppression component of the present invention generally have a molecular weight that will render the polyglycol  
20 sufficiently water soluble or poorly water insoluble and of proper viscosity so as not to inhibit preparation and handling. Generally for most polypropyleneglycols, this means a molecular weight in the range of about 100 to about 1200. Accordingly, it is believed that for most polyglycols, a molecular weight above about 1200 will have a tendency to be water insoluble or at least not sufficiently water soluble for use in  
25 the present invention. Of course, in those instances where a certain polyglycol may have a molecular weight outside of the above range and still be suitable, it may certainly be utilized.

5 Polypropylene glycols having a molecular weight in the range of about 200 to about 600 are most preferred for use as the alcohol component of the present invention.

The relative amounts of the components of the well fluid additive of the present invention are generally selected to provide compatibility with each other and  
10 with the well fluid, to provide suitable shale, clay or fines stabilization, and to inhibit, suppress or delay the formation of gas hydrates.

Generally, based on the total weight of the well fluid additive, the well fluid additive of the present invention will comprise in the range of about 0.1 to about 99 weight percent polymer component and in the range of about 1 to about 99.9 weight  
15 percent hydrate suppression component, based on the total weight of the polymer component and the hydrate suppression component. Preferably, the well fluid additive of the present invention will comprise in the range of about 0.5 to about 10 weight percent polymer component, and in the range of about 90 to about 99.5 weight percent hydrate suppression component, based on the total weight of the  
20 polymer component and the hydrate suppression component. More preferably, the well fluid additive of the present invention will comprise in the range of about 1 to about 5 weight percent polymer component, and in the range of about 95 to about 99 weight percent hydrate suppression component, based on the total weight of the polymer component and the hydrate suppression component. Most preferably, the  
25 well fluid additive of the present invention will comprise in the range of about 1 to about 3 weight percent polymer component, and in the range of about 97 to about 99 weight percent hydrate suppression component, based on the total weight of the polymer component and the hydrate suppression component.



5 In the practice of the present invention, the well fluid additive is generally added to the well fluid in an amount in the range of about 0.35 to about 280 pounds/ bbl well fluid, thus comprising in the range of about 0.1 to about 80 weight percent of the well fluid. Preferably, the well fluid additive is added to the well fluid in an amount in the range of about 3.5 to about 175 pounds/ bbl well fluid, thus  
10 comprising in the range of about 1 to about 50 weight percent of the well fluid. More preferably, the well fluid additive is added to the well fluid in an amount in the range of about 7 to about 70 pounds/ bbl well fluid, thus comprising in the range of about 2 to about 20 weight percent of the well fluid. Most preferably, the well fluid additive is added to the well fluid in an amount in the range of about 17.5 to about 35 pounds/  
15 bbl well fluid, thus comprising in the range of about 5 to about 10 weight percent of the well fluid.

It is to be understood that other additives used by those of skill in the art may also be added to the drilling fluids of the present invention, as long as they do not have a substantial detrimental effect on the well fluid, including but not limited to for  
20 example, surfactants, weighting materials, breakers and loss circulation additives.

### EXAMPLES

The following examples are provided merely to illustrate embodiments of the present invention and are not meant to limit the scope of the claims of the invention  
25 in any way.

The poly(vinyl alcohol) ("PVA") used in these examples was Airvol 540 S, commercially available from Air Products, and having a molecular weight of 100,000 g/mol. The polymer was used by first making a 20 % by weight solution in

5 water. The poly(vinyl pyrrolidone) ("PVP") used in these examples was Luviskol K-90, commercially available from BASF with a molecular weight of 1,000,000 g/mol. Versa TL 502 is polystyrene sulfonate with a molecular weight of 500,000 g/mol sold by National Starch and Chemical Company. Gafquat 755 N is a copolymer of vinylpyrrolidone and dimethylaminoethyl methacrylate available from International  
10 Specialty Polymers. Natrosol 250 NHR is a hydroxyethyl cellulose viscosifier available from Hercules, Inc. PERMALOSE HT is made from carboxymethyl starch, Biolose is a derivatized starch, and XC-polymer is made from xanthan gum. A3192, A3274, AQUACOL D are polypropylene glycols available from Baker Hughes Inteq. Biozan is a biopolymeric viscosifier available from Kelco. DP/TP 213C is a  
15 terpolymer of Acrylamide, acrylate and AMPS in a mole ratio of 70/15/15, obtained from HYCHEM, Inc. Geo-Meg is methyl glucoside. Sample # 907-12-1 and 908-29-1 were synthesized by the inventors and are a copolymer of acrylamide and vinylpyrrolidone. Geo - Meg 207 is methyl glucoside available commercially from Horizon Co. Samples 8069:115A and 8069:115B are copolymers of styrene  
20 sulfonate and methyl methacrylate, were obtained from National Starch Chemical Company, and used as received (25 and 27 % by weight in water, respectively).

Glass pint jars were used to obtain the rolling erosion data. The mud components were blended in the compositions listed as shown in the tables utilizing a multimixer. Rheological properties were measured using a FANN 35 viscometer.

25 Fluid loss properties were measured using an API filtration apparatus.

All polymers were evaluated in a 25 % by weight calcium chloride mud. The solubility of the polymers in a 25 % by weight calcium chloride solution was evaluated by preparing the solution, then allowing the solution to roll at 150°F for 16

hours. Rolling erosion data was obtained using HOLE - PLUG (mined bentonite 3/8" in size, available from Baroid Corporation). To each mud sample was added 25 grams of HOLE-PLUG, with the mud samples subsequently screened through an 18- mesh sieve after rolling 16 hours at 150°F. The remaining HOLE-PLUG was washed, dried for four hours at 225°F and weighed. The percent erosion loss was calculated, assuming an initial moisture content of 8.8 %. When the wafer test was utilized to determine erosion loss, a procedure similar to the HOLE-PLUG procedure described above was used, except that for the wafers a 12 % initial moisture content was used to do the % erosion loss calculations. The erosion loss wafers were made from Gulf of Mexico gumbo shale. The amount of materials used and the composition of each mud along with the properties are described in the following Tables 1- 7.

Besides calcium chloride, all test polymers were also evaluated in other brines composed of sodium chloride, potassium chloride or sodium formate. All brine formulations were designed for the lowest freezing points, a necessary factor routinely considered for gas hydrate suppression in deep water drilling. Glycols, another class of additives well known for freezing point depression, were also evaluated for any potential synergistic effects in shale stabilization.

The results of the Examples are listed in the following Tables 1-7, with the "A" portion of the tables showing the mud composition, and the "B" portion of the tables showing the rheological properties of the various muds after dynamic aging at 150°F for 16 hours.

The following Table 1 summarizes the % erosion losses obtained for muds prepared with several polymers in calcium chloride. Comparing sample 2 with

sample 1 and 3, it can be seen that Versa TL 502 and Gafquat 755N act as encapsulants since the values of the % erosion data are reduced considerably (17 vs 10 and 2 %). Comparing sample 4 and sample 5 it can also be seen that addition of PVP reduces the % erosion losses to 0 % from 9 %. Sample 6 and sample 7 show that 0 % erosion can be obtained with Airvol 540S and with the terpolymer DP/TP 213C. These muds exhibited good filtration control.

**TABLE 1-A: Evaluation of Polymers as Shale Encapsulants in Calcium Chloride(25 %) Muds**

Sample #	1	2	3	4	5	6	7
Water, ml	350	350	350	350	350	350	292
Calcium Chloride, g	89	89	89	89	89	89	89
Caustic, g	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Airvol 540S, g	-	-	-	-	-	-	2
Luvskol K-80, g	-	-	-	2	-	-	-
Versa TL- 502, g	-	-	2	-	-	-	-
Gafquat 755N, g	2	-	-	-	-	-	-
DP/TP 213C, g	-	-	-	-	-	2	-
Biolose, g	-	-	-	-	-	-	4
XC-polymer, g	-	-	-	-	-	-	1.2
Natrosol 250NHR, g	1	1	1	1	1	-	-
Permalose HT, g	4	4	4	6	6	6	-
Biozan, g	1	1	1	1	1	1	-
Barite	204	204	204	204	204	204	204

**TABLE 1-B: Rheological Properties of Muds After Dynamic Aging at 150°F for 16 hours w/25 g HOLE-PLUG**

Sample #	1	2	3	4	5	6	7
600	74	62	69	70	87	37	42
300	39	39	41	40	57	20	25
PV	35	23	28	30	30	17	17
YP	4	16	13	10	27	3	8
10-S	2	3	2	2	3	2	4
10-M	2	3	2	2	3	2	3
API, ml	10	6	4	4	2	10	0.2
% Erosion	2	17	10	0	9	0	0

The following Table 2 shows that the addition of a glycol improves the shale stability in PVA/Calcium chloride muds. Comparing sample 2 and sample 3 it can be seen that a synergistic effect is found. Sample 1 and 3 have high API values. When Biolose was used as a filtration control agent with PVA (samples 5-8), good API values were obtained. In this system, all glycols studied gave 0 % erosion.

**TABLE 2-A: Evaluation of Poly(vinyl alcohol)/ Calcium Chloride Mud Containing Glycols.**

Sample #	1	2	3	4	5	6	7	8
Water, ml	301	301	301	301	292	292	292	292
MgCl <sub>2</sub> , g	-	-	-	100	-	-	-	-
CaCl <sub>2</sub> , g	89	89	89	-	89	89	89	89
Caustic, g	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Airvol 540S, g	2	2	-	2	2	2	2	2
Biolose, g	-	-	-	-	4	4	4	4
XC-polymer, g	-	-	-	-	1.2	1.2	1.2	1.2
Natrosol 250 NHR, g	2	1	1	1	-	-	-	-
Blozan, g	1	1	1	1	-	-	-	-
Barite, g	204	204	204	204	204	204	204	204
A-3192, ml	17.5	17.5	17.5	17.5		17.5		
A-3274	-	-	-	-	-	-	17.5	-
Aquacol D, g	-	-	-	-	-	-	-	17.5
Perma-Lose HT, g	-	2.0	2.0	2.0	-	-	-	-

**TABLE 2-B: Rheological Properties of Mud After Dynamic Aging at 150°F for 16 Hours w/ 25g HOLE-PLUG**

Sample #	1	2	3	4	5	6	7	8
600	134	67	71	136	42	32	25	48
300	85	39	43	88	25	16	13	27
PV	49	28	28	48	17	16	12	21
YP	36	11	15	40	8	0	1	6
10 - S	4	2	2	9	4	2	3	4
10 - M	6	3	3	16	3	2	3	4
API, ml	50	1.0	24	1.6	0.2	0.2	0.2	2
% Erosion	0	0	12	0	0	0	0	0

The following Table 3 summarizes the effect of adding A3274 glycol and methyl glucoside to all the polymers tested. All samples exhibited 0% erosion, reasonable rheological properties, and good filtration control.

**TABLE 3-A: Effects of glycols and Methyl Glucoside on Shale Encapsulating Power of Polymers in CaCl<sub>2</sub> Muds**

Sample #	1	2	3	4	5	6	7	8	9	10	11	12
Water, ml	350	350	350	350	350	350	350	350	350	350	350	350
CaCl <sub>2</sub> , g	89	89	89	89	89	89	89	89	89	89	89	89
Caustic, g	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Airvol 540S, g	2	-	-	-	-	2	-	-	-	-	-	-
Luviskol K-90, g	-	2	-	-	-	-	2	-	-	-	-	-
DP/TP 213C, g	-	-	2	-	-	-	-	2	-	-	-	-
Gafquat 755N, g	-	-	-	2	-	-	-	-	2	-	-	-
907 - 12 - 1, g	-	-	-	-	2	-	-	-	-	2	-	-
Versa TL 502, g	-	-	-	-	-	-	-	-	-	-	2	2
Perma-Lose, HT, g	4	4	4	4	4	4	4	4	4	4	4	4
Natrosol 250NHR, g	1	1	1	1	1	1	1	1	1	1	1	1
Biozan, g	1	1	1	1	1	1	1	1	1	1	1	1
Barite, g	204	204	204	204	204	204	204	204	204	204	204	204
A-3274	7.5	17.5	17.5	17.5	17.5	-	-	-	-	-	-	-
Geo-Meg 207, g	-	-	-	-	-	12.2	12.2	12.2	12.2	12.2	-	12.2

**TABLE 3-B: Rheological Properties of Muds After Dynamic Aging at 150°F for 16 Hours w/ 25g HOLE-PLUG**

Sample #	1	2	3	4	5	6	7	8	9	10	11	12
600	41	59	132	53	102	66	80	140	70	80	55	62
300	24	34	75	30	63	41	45	68	41	48	32	36
PV	17	25	57	23	39	25	35	72	29	32	23	26
YP	7	9	18	7	24	16	10	4	12	16	9	10
10 - S	2	2	3	2	3	3	2	3	3	3	3	3
10 - M	2	2	3	3	3	3	3	3	3	3	3	3
API, ml	12	6.0	2.0	6.0	2.0	2.0	2.8	2.0	2.0	2.0	2.0	2.0
% Erosion	0	0	0	0	0	0	0	0	0	0	0	0

According to the following Table 4, the wafer test confirms the data of the above tables. Sample numbers 1, 3 and 5 were done in duplicate. Comparing sample 5 and sample 6, with sample 1 and sample 2, it can be seen that addition of the  $\text{CaCl}_2$  leads to better shale stability. Addition of Natrosol 250 HMR gives higher rheology as expected since it functions as a viscosifier. Sample number 3 and sample number 4 containing New Drill Plus in 20 % sodium chloride solution provided the same % erosion values as poly(vinyl alcohol) in calcium chloride.

**TABLE 4-A: Performance Evaluation of Poly(vinyl alcohol) and NEW DRILL PLUS in Different Brines Using the Wafer Test**

Sample #	1	2	3	4	5	6	7
Water, ml	301	301	301	301	301	301	301
$\text{CaCl}_2$ , g	-	-	-	-	89	89	89
Sea Salt, g	13	13	-	-	-	-	-
$\text{NaCl}$ , g	-	-	70	70	-	-	-
Caustic, g	0.25	0.25	0.5	0.5	0.5	0.5	0.5
New Drill Plus, g	-	-	2	2	-	-	-
Airvol 540 S, g	2	2	-	-	2	2	2
Biozan, g	1.25	1.25	0.5	0.5	-	-	1.0
Natrosol 250 HMR, g	-	-	-	-	1.5	1.5	1.0
Perma-Lose, HT, g	-	-	-	-	-	-	2.0
A-3192, ml	-	-	-	-	-	-	17.5

**TABLE 4-B: Rheological Properties of Solutions After Dynamic Aging at 150°F for 16 Hours with Wafers**

Sample #	1	2	3	4	5	6	7
600	20	20	28	28	50	50	58
300	16	16	20	20	30	30	36
PV	4	4	8	8	20	20	22
YP	12	12	12	12	10	10	14
% Erosion	19.4	23.4	0.6	0.0	0	0	0

All samples tested in the following Table 5 showed that in 20 % sodium chloride muds, addition of a glycol reduces the percent erosion losses considerably.

The following Table 6 summarizes the effect of adding glycols in 20 % sodium chloride to poly(vinylpyrrolidone -co- acrylamide) and poly(styrene sulfonate-co-methyl methacrylate). According to this data, only the polymer labelled as 8068:115B shows some improvement in shale stability by adding glycol (sample 5 vs sample 6).

According to the following Table 7 good shale stability and good rheological properties are obtained with polymers in sodium formate and potassium chloride make up waters.

**TABLE 5-A: Evaluation of Polymers in 20 % Sodium Chloride With and Without Glycols**

Sample #	1	2	3	4	5	6	7	8	9	10
Water, ml	300	300	300	300	300	300	300	300	300	300
NaCl, g	70	70	70	70	70	70	70	70	70	70
Caustic, g	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Luviskol K-90, g	-	-	2	2	-	-	-	-	-	-
DP/TP 213 C, g	2	2	-	-	-	-	-	-	-	-
Gafquat 765N, g	-	-	-	-	2	2	-	-	-	-
Versa TL 602, g	-	-	-	-	-	-	2	2	-	-
New Drill Plus, g	-	-	-	-	-	-	-	-	2	2
Milpac, LV, g	2	2	2	2	2	2	2	2	2	2
Biozan, g	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Barite, g	204	204	204	204	204	204	204	204	204	204
AQUACOL, ml	17.5	-	-	17.5	-	17.5	-	17.5	-	17.5



**TABLE 5-B: Rheological Properties of Muds After Dynamic Aging at 150°F with HOLE-PLUG ( 25 grams)**

Sample #	1	2	3	4	5	6	7	8	9	10
600	132	86	77	103	130	129	75	58	190	250
300	85	48	45	60	77	70	43	32	112	145
PV	47	38	32	43	53	59	32	26	78	105
YP	38	10	13	17	24	11	11	6	34	40
10-S	5	3	3	4	4	4	3	3	6	8
10-M	5	3	3	3	5	4	3	2	8	8
API, ml	4.0	4.0	10.0	14.0	8.0	6.0	3.0	14.0	2.0	2.0
% Erosion	0	39	5	2	7	4	17	5	2	1

**TABLE 6-A: Evaluation of Poly(vinylpyrrolidone-co-acrylamide) and Poly(styrene sulfonate-co- methylmethacrylate) as Shale Encapsulants in 20 % Sodium Chloride Muds**

Sample #	1	2	3	4	5	6
Water, ml	300	300	300	300	300	300
NaCL, g	70	70	70	70	70	70
Caustic, g	0.5	0.5	0.5	0.5	0.5	0.5
908-29-1,g	2	2	-	-	-	-
8068:115A, g	-	-	2	2	-	-
8068:115B,g	-	-	-	-	2	2
Milpac LV,g	1	1	1	1	1	1
Biozan,g	0.7	0.7	0.7	0.7	0.7	0.7
Barite,g	204	204	204	204	204	204
AQUACOL, ml	-	17.5	-	17.5	-	17.5

**TABLE 6-B: Rheological Properties of Muds After Dynamic Aging at 150°F for 16 Hours**

Sample #	1	2	3	4	5	6
600	45	48	37	90	35	30
300	23	25	20	75	20	12
PV	22	23	17	15	15	18
YP	1	2	3	60	5	6
10-S	2	2	2	3	3	2
10-M	2	2	2	3	2	2
API, ml	6.0	8.0	2.0	8.0	8.4	6.0
% Erosion	26	22	29	32	28	9.6

**TABLE 7-A: Evaluation of Polymers as Shale Encapsulants in Sodium Formate and Potassium Chloride Muds**

Sample #	1	2	3	4	5	6	7	8	9	10	11	12
Water, ml	301	301	301	301	301	301	315	315	315	315	315	315
Sodium Formate, g	60	60	60	60	60	60	-	-	-	-	-	-
Potassium Chloride, g	-	-	-	-	-	-	77	77	77	77	77	77
Lurviskol K-90, g	2	-	-	-	-	-	2	-	-	-	-	-
DP/TP 213B, g	-	2	-	-	-	-	-	2	-	-	-	-
Versa TL 502, g	-	-	2	-	-	-	-	-	2	-	-	-
New Drill Plus, g	-	-	-	2	-	-	-	-	-	2	-	-
Gafquat 766 N, ml	-	-	-	-	-	10	-	-	-	-	-	10
PermaLose, HT, g	2	2	2	2	2	2	2	2	2	2	2	2
Biozan, g	1	0.5	1	0.5	1	1	1	1	0.5	1	0.5	1
Barite, g	204	204	204	204	204	204	204	204	204	204	204	204

**TABLE 7-B: Rheological Properties of Muds After Dynamic Aging at 150°F for 16 hours w/ 25g HOLE-PLUG**

Sample #	1	2	3	4	5	6	7	8	9	10	11	12
800	79	94	71	86	58	71	37	46	57	44	50	60
300	53	66	50	60	43	50	27	33	38	32	35	40
PV	26	28	21	26	15	21	10	13	19	12	15	20
YP	27	38	29	34	28	29	17	20	19	20	20	20
10 - S	7	8	8	8	8	7	5	5	5	5	5	6
10 - M	9	10	10	10	10	9	7	7	7	7	7	8
API, ml	1.0	2.0	14	3	4.6	2.8	4.8	3.0	3.0	10	3.8	4.0
% Erosion	0	3	13	1	30	3	9	0	3	2	0	4

While the illustrative embodiments of the invention have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those skilled the art to which this invention pertains.

5

CLAIMS:

CLAIM 1. A drilling fluid additive comprising a polymer component and a hydrate suppression component, wherein the polymer component is selected from the group of polymers consisting of polyvinylalcohol, polyvinylpyrrolidone, polymer of styrene sulfonic acid, cationic polymers, terpolymers of acrylamide, acrylate, acrylamide  
10 propane sulfonic acid, and polyvinylpyrrolidone copolymers, and wherein the hydrate suppression component is selected from the group of agents consisting of salts, and water-soluble or poorly water insoluble alcohols and derivatives thereof.

CLAIM 2. The drilling fluid additive of claim 1 wherein the hydrate suppression  
15 component comprises a salt selected from the group of salts of calcium, magnesium, potassium, and sodium.

CLAIM 3. The drilling fluid additive of claim 2 wherein the hydrate suppression component comprises calcium chloride.

20

CLAIM 4. The drilling fluid additive of claim 3 wherein the polymer component is selected from the group of polymers consisting of polyvinylalcohol, polyvinylpyrrolidone, and polyvinylpyrrolidone copolymers.

25 CLAIM 5. The drilling fluid additive of claim 4 wherein the fluid comprises in the range of about 0.5 to about 10 weight percent polymer component, and in the range of about 90 to about 99.5 weight percent hydrate suppression component, based on the total weight of the polymer component and the suppression component.

5 CLAIM 6. The drilling fluid additive of claim 1 wherein the polymer component is selected from the group of polymers consisting of polyvinylalcohol and polyvinylpyrrolidone, and the hydrate suppression component is calcium chloride.

10 CLAIM 7. A water-based drilling fluid comprising an aqueous component, a polymer component and a hydrate suppression component, wherein the polymer component is selected from the group of polymers consisting of polyvinylalcohol, polyvinylpyrrolidone, polymer of styrene sulfonic acid, cationic polymers, terpolymers of acrylamide, acrylate, acrylamide propane sulfonic acid, and polyvinylpyrrolidone copolymers, and wherein the hydrate suppression component  
15 is selected from the group of agents consisting of salts and alcohols.

CLAIM 8. The drilling fluid of claim 7 wherein the hydrate suppression component comprises a salt selected from the group of salts of calcium, magnesium, potassium, and sodium.

20

CLAIM 9. The drilling fluid of claim 8 wherein the hydrate suppression component comprises calcium chloride.

CLAIM 10. The drilling fluid of claim 9 wherein the polymer component is selected  
25 from the group of polymers consisting of polyvinylalcohol, polyvinylpyrrolidone, and polyvinylpyrrolidone copolymers.

5 CLAIM 11. The drilling fluid of claim 10 wherein the fluid comprises in the range of about to about 0.5 to about 10 weight percent polymer component, and in the range of about 90 to about 99.5 weight percent hydrate suppression component, based on the total weight of the polymer component and the suppression component.

10 CLAIM 12. The drilling fluid of claim 7 wherein the polymer component is selected from the group of polymers consisting of polyvinylalcohol and polyvinylpyrrolidone, and the hydrate suppression component is calcium chloride.

CLAIM 13. A method a drilling in a subterranean formation situated in a hydrate  
15 prone environment and containing water-sensitive shales, clays and fines, the method comprising rotating a drill string to cut a borehole into the formation while circulating a water-based drilling fluid, having an aqueous component, a polymer component and a hydrate suppression component, down through the drill string and then up an annulus between the drilling string and the wall of the borehole, wherein  
20 the polymer component is selected from the group of polymers consisting of polyvinylalcohol, polyvinylpyrrolidone, polymer of styrene sulfonic acid, cationic polymers, terpolymers of acrylamide, acrylate, acrylamide propane sulfonic acid, and polyvinylpyrrolidone copolymers, and wherein the hydrate suppression component is selected from the group of agents consisting of salts and alcohols.

25

CLAIM 14. The method of claim 13 wherein the hydrate suppression component comprises a salt selected from the group of salts of calcium, magnesium, potassium, and sodium.

- 5 CLAIM 15. The method of claim 14 wherein the hydrate suppression component comprises calcium chloride.

- CLAIM 16. The method of claim 15 wherein the polymer component is selected from the group of polymers consisting of polyvinylalcohol, polyvinylpyrrolidone, and  
10 polyvinylpyrrolidone copolymers.

- CLAIM 17. The method of claim 16 wherein the fluid comprises in the range of about 0.5 to about 10 weight percent polymer component, and in the range of about 90 to about 99.5 weight percent hydrate suppression component, based on the total  
15 weight of the polymer component and the suppression component.

- CLAIM 18. The method of claim 13 wherein the polymer component is selected from the group of polymers consisting of polyvinylalcohol and polyvinylpyrrolidone, and the hydrate suppression component is calcium chloride.

# INTERNATIONAL SEARCH REPORT

International Publication No.  
PCT/US 95/09443

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C09K7/02 E21B37/06

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C09K E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	EP-A-0 668 339 (BAKER-HUGHES INC.) 23 August 1995 see page 5, line 54 - line 57 see page 3, line 45 - page 5, line 23 see page 2, line 1 - line 4 ---	1, 7, 13
Y	GB-A-2 216 574 (SHELL INTERN.MAATSH.) 11 October 1989 see page 3, line 6 - page 4, line 19; claims 3-10 ---	1, 2, 7, 8, 13, 14
Y	US, A, 5 076 364 (SHELL OIL COMP.) 31 December 1991 see column 2, line 19 - line 66 see column 14, line 32 - line 38; claims 1, 4-6, 10 ---	1-3, 7-9, 13-15
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

6 November 1995

Date of mailing of the international search report

27. 11. 95

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International Publication No  
PCT/US 95/09443

## C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	US-A-4 637 882 (D.G.PEIFFER) 20 January 1987  see column 4, line 22 - line 60 see column 1, line 36 - column 3, line 18 ---	1-4, 6-10, 12-16, 18
Y	US-A-5 076 373 (A.H.HALE) 31 December 1991 cited in the application see column 1, line 52 - column 2, line 5 see column 2, line 40 - column 3, line 48 see column 12, line 6 - line 46; tables 4, 5 ---	1, 2, 7, 8, 13, 14
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Y	US-A-4 609 476 (I.J.HEILWEIL) 2 September 1986  see column 2, line 61 - column 3, line 64 see column 5, line 7 - line 10 see column 6, line 1 - line 55 ---	1-4, 6-10, 12-16, 18
Y	FR-A-2 185 745 (SHELL INTERN. MAATSCH.) 4 January 1974 see page 4, line 27 - page 5, line 31 see page 8, line 17 - line 32; claims 1-8 -----	1, 2, 7, 8, 13, 14

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Information on patent family members

Internati

Application No

PCT/US 95/09443

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